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## (54) Heat-shrinkable elastomer production

(57) A method of producing a heat-shrinkable elastomer comprising the steps of:

(a) without the application of external heat, extending an elastomer comprising a copolymer of alternating polyamide and polyether repeat block polymer segments to an extension beyond that at which permanent deformation occurs thereby to orient said elastomer uniaxially, and (b) subsequently releasing the tension on said elastomer to allow natural relaxation thereof to a linear density substantially above the minimum linear density achieved in the extension of step (a) and substantially below that of said elastomer before the extension of step (a). Upon subsequent application of heat, the elastomer shrinks and recovers its elastic properties. Articles or garments such as disposable diapers advantageously use the heat-shrinkable elastomer of the present invention as a means to shirr portions thereof, such as waistbands.

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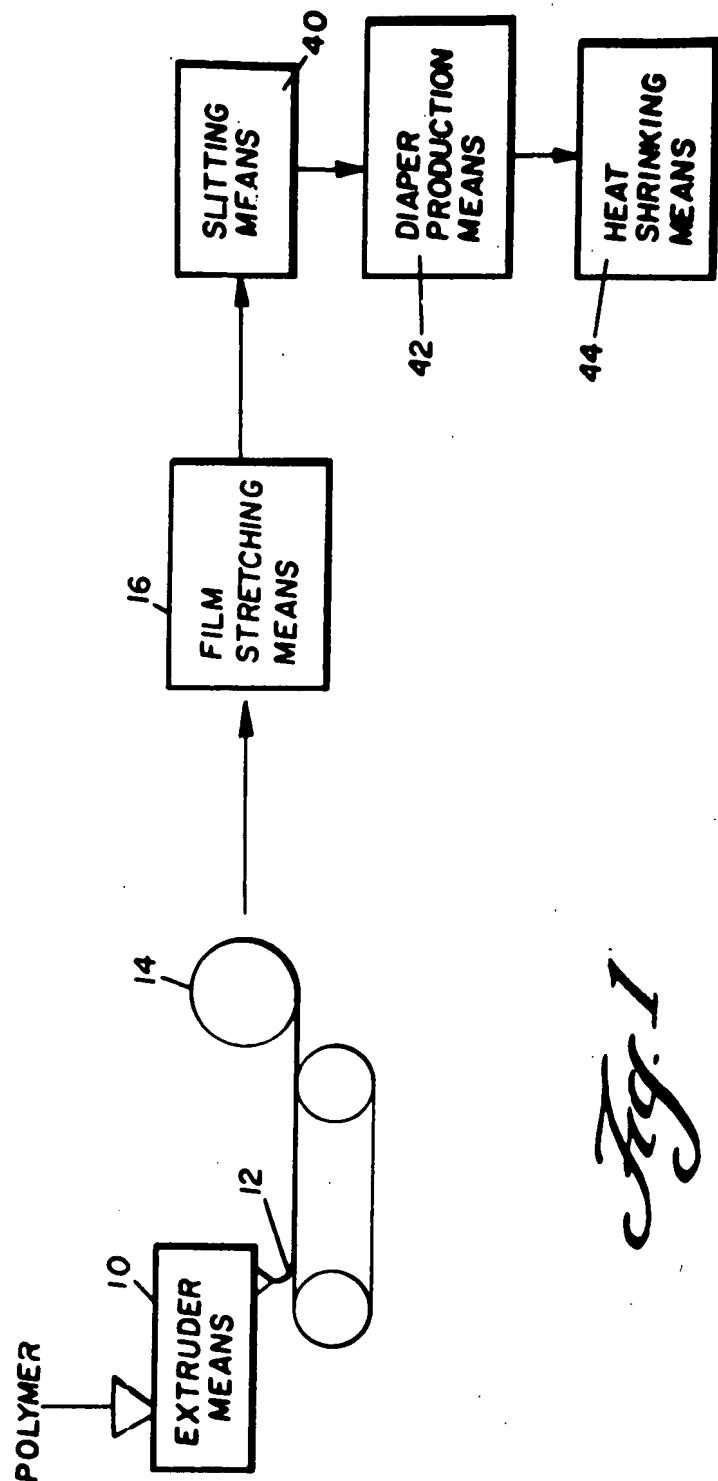
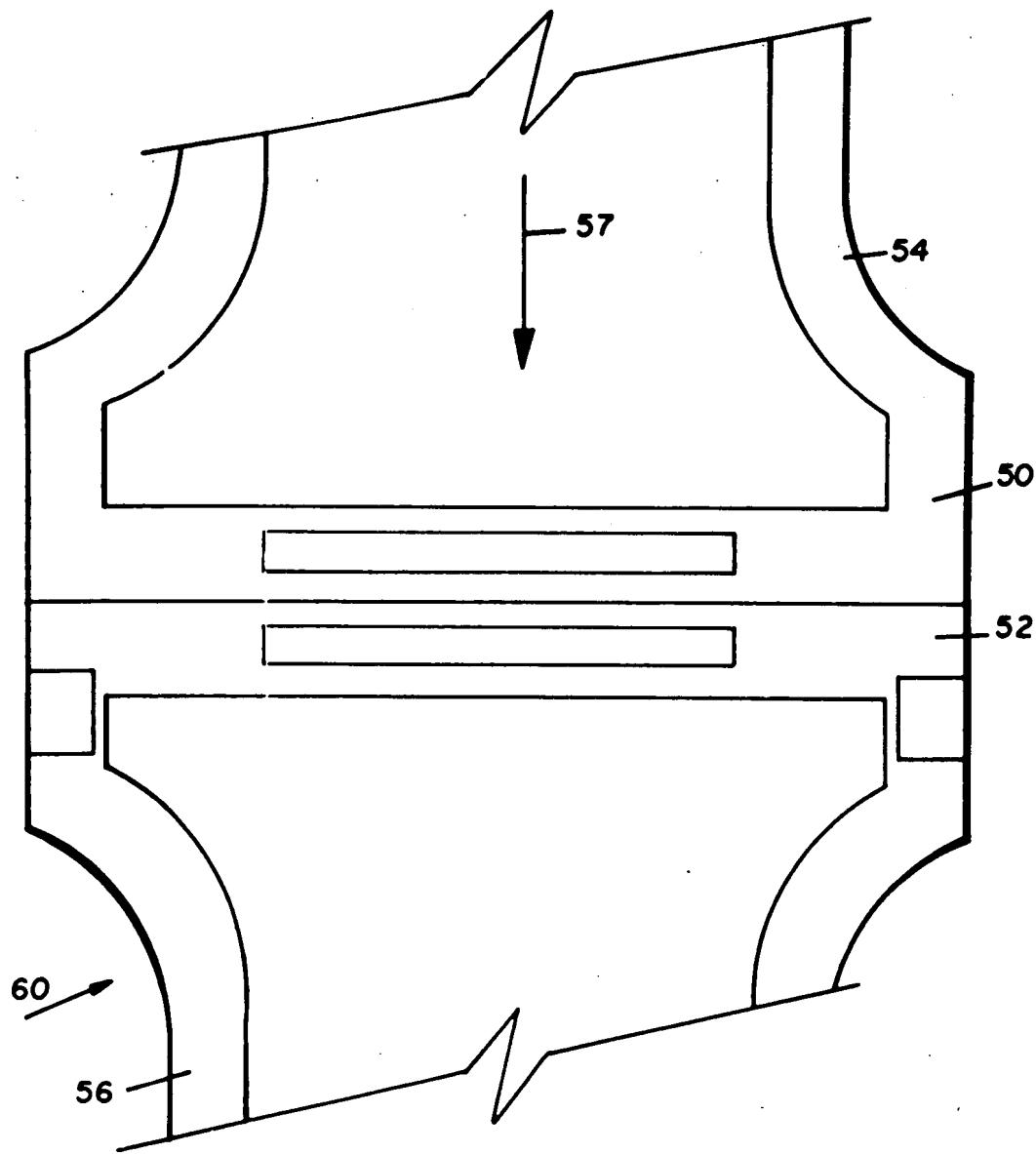


Fig. 1

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*Fig. 2*

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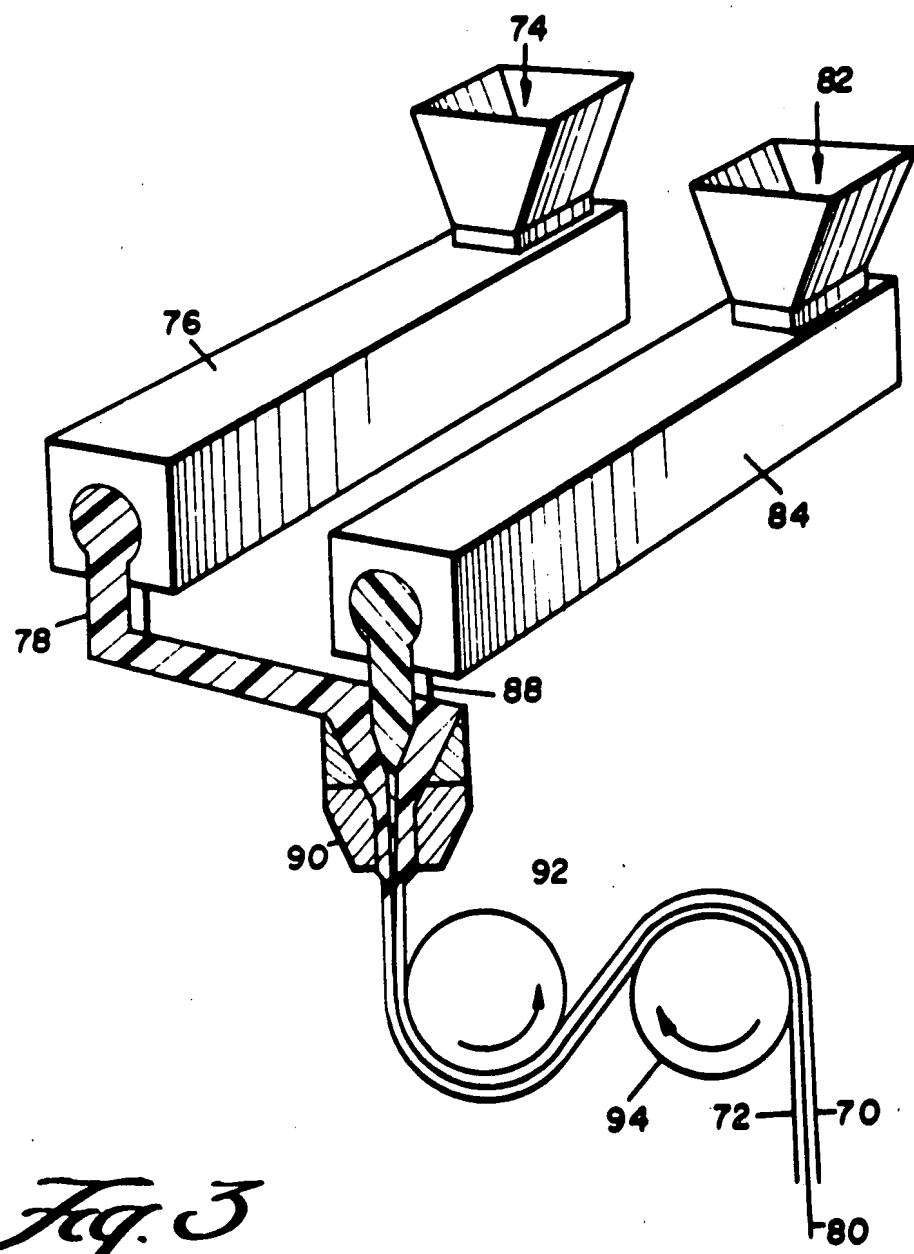


Fig. 3

## SPECIFICATION

## Heat-shrinkable elastomer production

## 5 Field of invention

The present invention relates to heat-shrinkable elastomers, and in its more specific aspect to heat-shrinkable elastomers especially useful for elastic shirring in garments, such as disposable diapers or like incontinence products.

## 10 Background of the present invention

Elastic shirring of the garments in selected regions is desirable or essential in order that the garment will conform to the body of the wearer such as at the waist or wrist. This feature is especially true with respect to disposable garments, including plastic garments such as disposable diapers. Hence, the invention, its background and several embodiments, will be described with particular reference to disposable diapers or incontinence garments, but it is understood that the invention is applicable to other garments such as gowns, masks, shoe covers, etc.

Disposable diapers typically have an "hour glass" or general "I-shaped" configuration. The diapers are produced from a continuous web of inner and outer facing sheets and an absorbent batt wherein each waistband area of a diaper module is integrally connected to the waistband area of immediately adjacent diaper modules. (In this regard, see FIGURE 2 of the accompanying drawings). The web is cut at the waistband area transverse to the web travel direction to thereby form individual diapers. Thus, the waistband is cut in a cross-machine direction.

Application of elastomeric material to the legbands of disposable diapers has been commercially achieved. However, when elastomeric material is attempted to be applied to waistbands on the same diaper having the legband attached, significant production problems arise. For example, if tension is maintained in the legband direction, the elastomer attached to the waistband tends to bunch the diaper and thus interfere with folding, packaging or other production sequences. We know of no commercial solution to the production problems described above.

Recently, certain proposals have been made regarding heat-set, heat-shrinkable elastomeric materials 30 for use in effecting shirring of disposable garments such as disposable diapers or hospital gowns as evidenced by U.S. Patent Nos. 3,912,565; 3,819,401; and 3,639,917.

U.S. 3,912,565 to Koch et al and U.S. 3,819,401 to Massengale et al disclose that flexible polyurethane and plasticized vinyl chloride sheet materials, respectively, are heated, stretched, and cooled to prevent premature shrinkage. In order to prevent premature shrinkage, the elastomeric sheet materials are again 35 heated to permit limited relaxation and cooled to heat set the sheet materials. The heat set sheet materials are then applied to articles and upon application of heat, they shrink to their original lengths thus shirring the articles. As more fully explained with reference to Figure 1 in Koch et al and Massengale et al, the sheet material is stretched between heated roll 25 and nip rolls 31, 33 then cooled, partially relaxed in heated liquid bath 45 and collected in roll 49. What should be noted in Koch et al and Massengale et al is that stretching is accomplished by application of external heat, cooled at the stretched condition, then again heated by application of external heat to effect controlled heat shrinkage.

U.S. 3,639,917 to Althouse discloses an elastomer comprising block copolymers that are heat-shrinkable. According to Althouse, the block copolymers are expanded or deformed from an original length at elevated temperatures to achieve a new length and then cooled to maintain the copolymers at the new 45 length in the expanded state. The copolymers of Althouse therefore retain the new length when cooled until again heated at which time shrinkage to the original length occurs. The copolymers of Althouse therefore are expanded from their original length to a new length, maintained at the new length by cooling, and subsequently returned to the original length upon application of heat.

## 50 Summary of the invention

In one aspect the invention thus provides a method of producing a heat-shrinkable elastomer comprising the steps of:

(a) without the application of external heat, extending an elastomer comprising a copolymer of alternating polyamide and polyether repeat block polymer segments to an extension beyond that at which permanent deformation occurs thereby to orient said elastomer uniaxially, and (b) subsequently releasing the tension on said elastomer to allow natural relaxation thereof to a linear density substantially above the minimum linear density achieved in the extension of step (a) and substantially below that of said elastomer before the extension of step (a).

In one preferred embodiment of the method of the invention, steps (a) and (b) comprise:

60 (a) uniaxially orienting an elastomer of a first length consisting essentially of a copolymer of alternating polyamide and polyether repeat block polymer segments, said orienting being conducted without the application of external heat to uniaxially orient said elastomer to a second length substantially greater than a third length at which permanent deformation of said elastomer occurs; and

(b) releasing the uniaxial tensioning applied according to step (a) to allow said elastomer to naturally 65 relax to said third length which is substantially greater than said first length.

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In a further preferred embodiment of the method of the invention, prior to step (a), a core of said elastomer is provided with an outer layer of an extendable nonelastomer.

In other aspects, the invention provides a heat-shrinkable elastomer whenever produced by the method of the invention, a process for producing an elastomer which comprises the step of heat-shrinking such a 5 heat-shrinkable elastomer, and an article having a portion thereof elastically shirred by the attachment thereto of such a heat-shrunk elastomer.

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The elastomer of the present invention which exhibits potential elastic energy recoverable upon heat-shrinking is oriented as by stretching or rolling in one direction without the application of external heat to a length so that when the applied tension is removed, the elastomer relaxes to a permanent deformation 10 length greater than the original length yet less than the stretched length. More significantly, the heat-shrinkable elastomer having an original or first length is stretched in one direction to a substantially greater or second length without the application of external heat as, for example, to at least about 200%, preferably at least about 200 to at least about 700%. When relaxed, the elastomer assumes a permanent deformation at a third length somewhere between or somewhat intermediate to the first and second 15 lengths. This third length or intermediate state is sometimes known as a preform. The tensioned elastomer including the preform exhibits reduced elastic properties while in the deformed state. Upon the subsequent application of heat, the elastomer shrinks and recovers or assumes its elastic properties. The elastomer, when tensioned at practical or preferred values, exhibits an increase in permanent deformation length with increased tension whereas the conventional elastomers exhibit minimal permanent deformation. 20

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It is significant that heat-setting and cooling of the elastomeric preform is obviated. Tensioning and relaxing the elastomer, which apparently results in uniaxial orientation of the polymer, is performed without the application of external heat, that is at room temperature or ambient conditions (e.g. 70-75°F (21.1 to 23.9°C)) although an internal rise in temperature occurs. However, the elastomer retains its heat-shrinkable characteristics. Thus, certain processing steps and associated equipment are eliminated in the 25 commercial application of the elastomer to a garment.

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In accordance with one embodiment of the invention, the elastomer is coextruded or laminated with a nonelastomer, a nonelastic material. Preferably, the elastomer and the nonelastic are coextruded as a composite sheet, e.g. according to known techniques. Most desirably, the composite comprises three layers - an intermediate elastomeric layer and two outer layers. The elastomer may exhibit tackiness and on standing as in roll form may block. The skin layer of nonelastic is selected to provide non-blocking or release when the material is unrolled, which facilitates processing, such as, guiding, cutting and placement. Further, the elastomer may exhibit poor or no adhesion to many garment materials. Therefore, the oppositely disposed outer layer of the composite which faces the garment is affixed to the garment as 30 35 with a pressure sensitive or heat-sensitive adhesive. Thus, the composite has these advantages not possessed by the single layer composite.

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In a further aspect, the invention provides a process of elasticating an article comprising affixing to said article a heat-shrinkable elastomer produced according to the method of the invention, and preferably further comprising the step of heat-shrinking the affixed elastomer to cause shirring of said article. 40

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Preferred embodiments of the invention will now be described by way of Example and with reference to the accompanying drawings, in which:

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Figure 1 is a block diagram representing the processing steps of the present invention;

Figure 2 is a schematic plan view of a portion of a continuous diaper web during manufacture having ribbons of the film of the present invention attached to the waistband area thereof and shown prior to 45 being heat-shrunk; and

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Figure 3 is a schematic view of a means to coextrude the multilayer film embodiment of this invention.

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#### *Detailed description of the preferred exemplary embodiments*

##### *1. Single Layer Film Embodiment*

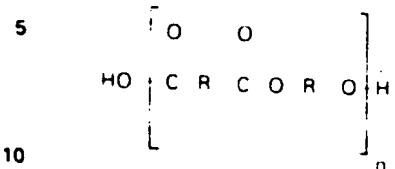
50 Referring to FIGURE 1, it is seen that the process of the present invention begins with the extrusion of the polymer which may initially be in pellet form by conventional extrusion means 10 to form a film 12 which is preferably subsequently stored in rolls 14 and transported to the next processing station e.g. film stretching 16. Advantageously, the extruded film has a thickness of between about 2 mils to about 4 mils (about 51-102 µm), although other thicknesses are possible in dependence upon the amount of 55 stretching that is needed to achieve the desired degree of article shirring, the specific polymer that is used, the economics of production or the like.

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While the term "film" has been used above, the elastomers of the present invention can be produced in other structural forms such as ribbon, thread, tape or the like. For convenience of reference, however, the term "film" will be used hereinafter.

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The polymer used to produce the film in accordance with the present invention is preferably a block copolymer having alternating segments of polyamide and polyether block polymers according to the general formula:



wherein R<sub>1</sub> represents the polyamide polymer block exemplified by nylon 6, nylon 6,6, nylon 10, nylon 11, and nylon 12 and R<sub>2</sub> represents the polyether polymer block exemplified by polyethylene glycol, polypropylene glycol and polytetramethylene glycol and wherein n is an integer. The copolymers in accordance with the above description are commercially available from the Rilsan Corporation of Glen Rock, New Jersey, USA under the trade name PEBAK. Particularly preferred for the films of the present invention are the PEBAK extrusion grades 2533 and 3533.

The film 12 formed as described previously is then subjected to uniaxial stretching without application of external heat, conveniently by any conventional film stretching means 16 such as by the differential speed roll process. A particularly preferred differential speed roll suitable for use as film stretching means 16 to stretch films of the present invention is a Marshall and Williams Model D7700 machine direction stretching apparatus. According to well-known principles of differential roll stretching, the film 12 is uniaxially stretched due to the differential speed of low-and high-speed rolls. Another method of orientation to induce heat shrinking is by "cold rolling" on multistack rolling mills under external pressure similar to that used in rolling thin metal sheet such as aluminum foil. Regardless of the orientation method, however, the common phenomenon accomplished is an increase of the dimension in the direction of orientation and a corresponding decrease in thickness.

Conventional, uniaxially stretched polymeric films are typically pre-heated to a temperature at or above the second order phase transition temperature. The conventional film is then stretched while at such elevated temperatures and subsequently cooled while being maintained in its stretched condition. Such pre-heating is important to conventional films so as to ensure proper stretching and orientation thereof.

Preheating is completely unnecessary with the present invention, however. Some heat may be generated during the uniaxial stretching of the film 12 due to frictional forces or the like particularly if differential speed rolls are utilized to effect film stretching, but it has been surprisingly found that such 35 temperature is significantly below (e.g. substantially less than 175 F (79.4 C)) the temperature at which deformation relaxation of the copolymer film begins to occur. That is, even though some heat may be frictionally generated during film stretching, the temperature which the film of the present invention reaches is substantially below the temperature at which relaxation of the deformation occurs. Heat setting, of course, contemplates that the temperature must be at or above the temperature at which deformation relaxation begins to occur. (See, U.S. Patent 3,912,565 at column 3, lines 28-38.) Thus, no heat- 40 setting of the oriented film of the present invention is required in direct contrast to what was conventionally thought to be essential in this art.

The amount of uniaxial stretching of the elastomer films of this invention is important to achieve adequate shrinkage and thus shrinking of an article utilizing the film. In accordance with the present invention 45 uniaxial tensioning is accomplished so that the film is stretched to an elongated length significantly greater than that length at which permanent deformation occurs. Upon removal of the applied tension, the film will naturally relax (e.g. without being induced to relax by the application of heat) to a length greater than the original length, corresponding to the amount of permanent deformation which has been 50 impaired thereto. Thus, the differential length between the permanent deformation length and the original, pre-stretched length is available for heat shrinkage. Upon application of heat therefore (e.g. at or above 175 F (79.4 C)) the stretched film will further be induced to relax and shrink. That is, a large portion of the differential length of the stretched film between the original length and the permanent deformation length is present as permanent deformation which is capable of recovery upon application of heat.

55 The film of the present invention is conveniently uniaxially stretched to achieve between about 200% to about 700% elongation per unit length of the film. It has been discovered that when the film of the present invention is uniaxially stretched within the ranges noted above, it will exhibit some natural relaxation upon removal of the stretching force but such relaxation will not proceed below the respective permanent deformation length. The length of the film corresponding to the amount of permanent deformation 60 imparted thereto is therefore dependent upon the amount of uniaxial tensioning to which the film is subjected. However, for uniaxial stretching in the range of about 200% to 700%, the permanent deformation length will be between about 20% and 60% of the film's elongated length. That is, the amount of permanent deformation available for heat shrinkage will be about 20% to about 60% of the stretched length of the film when stretched between about 200% to about 700% (e.g. when stretched 3x to 8x of the original 65 length).

The amount of permanent deformation which is imparted to the film of the present invention will therefore determine the degree of heat shrinkage which is available to adequately shirr that portion of an article with which it is associated. It has been found that a permanent deformation of between about 20-60% of the elongated length (termed the "unrestricted shrinkage") will advantageously translate into between about 30-45% shrinkage (termed the "restricted shrinkage") when the uniaxially stretched film is attached to a portion of a flexible garment such as the waistband of a disposable diaper. That is, since the flexible article will interfere or restrict the shrinkage of the film somewhat, complete return to the original, prestretched film length does not occur upon heat shrinkage. Nevertheless, when the film of the present invention is uniaxially stretched as described above (e.g. between about 20-60% permanent deformation or elongation based upon the final elongation to which the film is subjected), desirable article shirring occurs.

Subsequent to stretching, the film of the present invention is advantageously slit by conventional film slitting means 40 along the direction of permanent deformation (that is, parallel to the uniaxial stretching direction) to form ribbons which are advantageously 3/8" to 1/2" (9.5 to 12.7 mm) wide but other widths are, of course, possible depending upon the intended application. The ribbons can then be level wound according to known techniques into spools for use in diaper production equipment 42.

The ribbons are preferably cut to desired lengths (advantageously about 6" (15.2cm)) while still in their heat-shrinkable elongated condition and adhesively secured to waistband portions 50, 52 of diapers 54, 56 as the connected web 60 travels in the machine direction (arrow 57 in FIGURE 2). Adhesives suitable for binding ribbons of the films of this invention to the waistband areas of the diapers are commercially available from the H.B. Fuller Co. under the designation HL-1307-33-1 and the Findley Co. under the designation X807-378-01. The ribbon can be cut to the desired length either before or after it is applied to the diaper, and a cohesive or adhesive can be applied to the diaper or to the elastomer ribbon prior to joining the ribbon and diaper together. Alternatively, the plastic ribbon may have an adhesive property within itself which is present when the ribbon is applied to the diaper or which is activated by other means, such as heat, solvents, pressure, etc. In addition, the waist band portion of the diaper may be selectively positioned along the manufacturing machine direction to facilitate the application of the ribbon.

It is presently contemplated that a stack of folded diapers (advantageously eight to ten diapers per stack) having ribbons of the heat-shrinkable elastomeric film of the present invention will be collectively subjected to heat by suitable heat shrinking means 44 so as to cause heat shrinkage of the ribbons to thus shirr the waistband portions of the diapers. Preferably, heat shrinkage of the ribbons in the diaper stack is accomplished according to the method described in our copending U.S. Patent Application Serial No. 605968 (and in copending British Patent Application No. 8511015 (Publication No. GB-A-1 535 350) a copy of the specification for which is on the file of the present application). In such a manner no interference with diaper folding equipment due to premature cross-machine gathering or shirring of the waistbands will occur.

## 2. Multilayer Film Embodiment

40 A further embodiment of the present invention resides in the coextrusion of the polyether polyamide copolymer described hereinabove with nonelastic polymers such as ethylene vinyl acetate (EVA), EVA ionomers such as Plexar 3, Plexar 102, and Surlyn 1702 (Plexar 3 and Plexar 102 are commercially available from the Chemplex Corporation while Surlyn 1702 is commercially available from DuPont), and polyethylene or the like to advantageously produce a film which is heat-shrinkable but yet exhibits a pleasing hand. Skin compatibility of elastic waistbands is desirable when the films of the present invention are used as waistbands for disposable diapers. According to this embodiment of the present invention, the polyether polyamide copolymer is coextruded as the core or intermediate layer with surface exposed layers or outer layers of nonelastic polymers. Although the outer layers may not be heat-shrinkable, they will not significantly affect the heat shrinkage of the core to such an extent that adequate shirring of the garment will not occur owing to the superior heat-shrinking capabilities of the core layer film.

The coextrusion of layers of diverse polymers or thermoplastic materials is, in and of itself, well known in the art as generally exemplified by U.S. Patent Nos. 3,557,265 to Chisholm et al and 3,479,425 to LeFevre et al. Coextrusion of diverse polymer materials is typically accomplished utilizing a multi-manifold coextrusion die or a single manifold with combining adaptors which permit the melt lamination of multiple layers of dissimilar polymer materials. One particularly preferred combining adaptor which can be advantageously employed to achieve coextruded films of this invention is described in U.S. Patent No. 4,152,387 to Cloeren.

55 A conventional means of producing coextruded multilayer films of this invention is schematically depicted in accompanying FIGURE 3. As shown therein the outer nonelastic layers 70, 72 are formed by melt extruding the nonelastic polymers 74 by means of extruder 76. Similarly, the elastic core layer 80 is formed by melt extrusion of the elastic polymer 82 (e.g. preferably PEBAK extrusion grades 2533 or 3533) by means of extruder 84. The melt extruded polymers 74, 82 are then passed to combining adaptor 90 via conduits 78, 88, respectively. As schematically shown, the elastic polymer 82 melt laminates with the nonelastic polymer 74 to form a core layer 80 of the elastic polymer 82 which is sandwiched between outer layers 70, 72 of the nonelastic polymer 74.

Although the temperature of the combining adaptor 90 is dependent upon the polymers utilized, it is preferable to maintain the temperature thereof between about 360 to about 500 F, preferably about 400 F (about 182.2 to 260.0 C, preferably about 204.4 C) to advantageously form the coextruded films of this invention. Additionally, it is preferable that the total thickness of the coextruded film be from about 2 to 5 about 5 mils (about 51 to 127  $\mu$ m) with from about 2 to about 4 mils (about 51 to 102  $\mu$ m) being particularly preferred, although other film thicknesses could be utilized in dependence upon the final stretched thickness that is desired. The coextruded film contacts chill rolls 92, 94 so as to cool it to substantially maintain the extruded thickness thereof. Another means for forming the multilayers is by blown coextrusion using a circular die with coaxial flow channels corresponding to the individual layers of the 10 composite. The coextruded film can then be oriented by conventional stretching means 16, slit into ribbons by slitting means 40, applied to diapers in diaper production means 42 and heat shrunk by heat shrinking means 44 as described above with reference to FIGURE 1.

The core layer of elastic polyether polyamide block polymer is preferably the major constituent (based 15 on percent of coextruded film by weight) present in the resulting coextruded film. The core layer therefore preferably is present in the coextruded film in an amount of from about 70% to about 90% by weight, with the balance conveniently being substantially evenly distributed between each of the outer 15 layers.

The behavior of the coextruded composite or laminate of this invention is similar to the behavior of the 20 single layer films described above. That is, when the composite is uniaxially oriented to a length of from about 200% to about 700% of the original length, permanent deformation will be imparted thereto at a length generally of from about 20% to about 60% of the elongated length. Upon removal of the tension force, the coextruded film will likewise naturally (i.e. without application of heat) relax to the length indicative of the permanent deformation imparted thereto (i.e. the permanent deformation length). Thus, the 25 differential in length between the elongated length and the permanent deformation length is available as a shrinkage length so that when heat is applied thereto (generally at temperatures near 175 F (79.4 C)) the film substantially relaxes and shrinks to recover its elastic properties.

As briefly noted above, the outer layers or skins of the composite tend to interfere somewhat with heat shrinkage of the overall film due to the nonelastic nature of the skins. However, such interference is not of a degree which masks the heat shrinkability of the composite. Since the outer layers are nonelastic, 30 uniaxial tensioning of the coextruded film also permanently deforms such outer layers. However, the overall coextruded film will still naturally relax to between about 20% to 60% of the elongated length upon removal of the tensioning force owing to the presence of the elastic core layer.

The intralaminar bonding strength between the outer layers and core layer is preferably at least 1200 35 grams in (463 N/m) to ensure that the layers remain laminated to one another when subjected to uniaxial orientation of up to about 700% elongation.

The use of microwave energy as the means to heat shrink both the single layer and multilayer film 40 embodiments of the invention is also possible. It has been discovered that when the elastomers of the invention are exposed to microwave energy of 2450 MHz and between 3-6 kilowatts for about 5-10 seconds, adequate heat shrinkage occurs. That is, when exposed to microwave energy the elastomers shrink 45 between about 20% to about 60% of the stretched length. For example, a particular heat-shrinkable elastomeric ribbon of this invention formed of a core layer of PEBAK extrusion grade 3533 coextruded with outer layers of Plexar 102 and uniaxially stretched to 4x the original length (e.g. 300% stretch) to achieve a ribbon thickness of 1.5 mils (38  $\mu$ m), exhibited at least 20% heat shrinkage when affixed to the inside wasitband area of a diaper when the ribbon-affixed diaper was exposed to microwave energy of 2450 45 MHz and between 3-6 kilowatts for about 5-10 seconds.

The following nonlimiting Examples further illustrate the invention.

#### Example 1

Single layer films were prepared from various commercially available polymers by the chill roll cast 50 method using a 36" (91.4 cm) extrusion die at die temperatures of 400-425 F (204.4-218.3 C) and at line speeds of 120 fpm (36.6 m/min) for 2 mil (51  $\mu$ m) and 60 fpm (18.3 m/min) for 4 mil (102  $\mu$ m) film. Heat shrinkability of film samples was examined by preparing 1" x 10" (2.5 x 25.4 cm) strips of film cut in the machine direction. The film samples were then marked at initial lengths of 4" (101.6 mm) and were conditioned at 72 F, 55% relative humidity for 24 hours. Subsequent to conditioning, individual samples 55 were stretched on an Instron Tensile Tester at 72 F (22.2 C) and 55% relative humidity to 100%, 300% and 500% elongation (i.e. 2X, 4X and 6X stretch). The initial jaw span of the Instron Tensile Tester was 4.5 inches (11.4 cm) which translated into film sample lengths of 9 inches (22.9 cm) at 100% elongation; 18 inches (45.7 cm) at 300% elongation and 27 inches (68.6 cm) at 500% elongation, respectively. In each instance, the rate of stretching was 1000 mm/min. The stretched samples were again conditioned at 72 F (22.2 C) and 55% relative humidity for 24 hours.

Permanent deformation was then measured as a percentage of the original 4 inch (10.2 cm) film length according to the formula:

$$5 \% \text{ Permanent Deformation} = \frac{L - L_0}{L_0} \cdot 100$$

wherein  $L_0$  represents the original film length and  $L$  represents the final length to which the film relaxes without application of heat after the applied tension is removed.

10 To determine the amount of heat shrinkability which is imparted to the films, the stretched film samples were then heat shrunk by subjecting the samples to 175 F (79.4 C) for 5 seconds. The length of each film sample subsequent to heat shrinkage ( $L_1$ ) was measured and the percent heat shrinkability was calculated by the formula:

$$15 \% \text{ Heat Shrinkability} = \frac{L_0 - L_1}{L_0} \cdot 100$$

wherein  $L_0$  is the length of the film as defined above with respect to percent permanent deformation.

20 In order to determine the elastic nature of the heat shrink materials, the hysteresis ratio of each sample was calculated using an Instron Tensile Tester equipped with an integrator unit. In each instance, the stretched and heat shrunk samples were secured between the jaws of the Instron Tensile Tester to establish a 4" (10.2 cm) initial length regardless of the sample size subsequent to heat shrinkage. Each sample was then stretched to 100% elongation at 500 mm min stretching rate. Thus all samples were elongated 25 to 8 inches (20.3 cm). During the elongation, the integrator unit measured the area under the stretch curve and the resulting data was noted. When 100% elongation occurred, the integrator unit was reset and relaxation of the Instron jaws was initiated until the initial 4 inch (10.2 cm) separation length was achieved. During relaxation, the integrator unit measured the area under the relaxation curve. The hysteresis ratio (HR) was therefore calculated as follows:

$$30 \text{ HR} = \frac{\text{Area under stretching curve}}{\text{Area under relaxation curve}}$$

Since a true elastomer (e.g. rubber) will exhibit a hysteresis ratio of about 1.0, measurement of the hysteresis ratios of the tested films provided an indication of their elasticity subsequent to heat shrinkage. Thus, single layer films which exhibited heat shrinkage of between about 40% to about 60% or more while yet having a hysteresis ratio of less than 2.0 were suitable for use as elastic waistbands for disposable diapers. The results are tabulated below in Table 1.

5

TABLE I

10	Sample No.	Film	Extruded Film Thickness	% Elongation	10
15	1	PEBAX-2533	4 mils (102 $\mu$ m)	0 100 300 500	15
	2	PEBAX-2533	2 mils (51 $\mu$ m)	0 100 300 500	
	3	KRATON 2703G	6 mils (152 $\mu$ m)	0 100 300 500	20
	4	KRATON 2109	5.9 mils (150 $\mu$ m)	0 100 300 500	
25	5	KRATON 2103	3 mils (76 $\mu$ m)	0 100 300 500	25
	6	TUFTANE-410 (51 $\mu$ m)	2 mils 100	0 300 500	
	7	NATURAL RUBBER (CONTROL)	12 mils (305 $\mu$ m)	0 100 300 400 500	35
	40				

Kraton is a trade name of the Shell Oil Co.

Tuftane is a trade name of Goodrich Chemical.

TABLE I (Continued)

Sample No.	% Permanent Deformation	% Heat Shrinkage	Hysteresis Ratio (H.R.)	
5				5
10	1	1.6	1.4	
	1.4	2.6	1.3	
	74.2	37.2	1.3	
15	261.0	63.9	1.3	
	2	3.9	1.4	10
	1.6	4.9	1.4	
	86.5	42.8	1.3	
20	268.0	65.4	1.3	
	3	5.1	3.2	15
	6.3	5.2	3.2	
	42.4	3.3	3.5	
	73.6	5.9	2.4	
25	4	5.5	1.7	
	3.5	7.0	1.7	20
	18.1	8.4	1.6	
	27.1	7.9	1.5	
30	5	9.7	1.6	
	1.1	11.6	1.6	
	2.9	13.1	1.6	
	4.1	12.9	1.7	
	6	0.5	1.80	
35	1.4	6.4	1.50	
	13.4	11.3	1.42	
	51.6	22.1	1.44	
	7	0	1.01	30
	1.4	1.0	1.05	
	2.4	1.0	1.07	
	5.3	2.0	1.05	
	6.3	2.0	1.08	
				35

inches (11.4 cm) which translated into film sample lengths of 9 inches (22.9 cm) at 100% elongation; 18 inches (45.7 cm) at 300% elongation and 27 inches (68.6 cm) at 500% elongation, respectively. In each instance, the rate of stretching was 1000 mm/min. The stretched samples were again conditioned at 72 F (22.2 C) and 55% relative humidity for 24 hours.

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**Example II**

Coextruded multilayer films having an elastomeric film core layer and nonelastomeric film outer layers were prepared using a conventional combining adaptor commercially obtained from the Cloeren Co. and was the type described in U.S. Patent 4,152,387. Testing for percent permanent deformation, percent heat 5 shrinkage and hysteresis ratio were conducted as in Example I, above, and the results are tabulated in Table II below.

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TABLE II

10	Sample No.	Film (Outer layer core /layer outer layer)	Extruded Film Thickness	% Stretch	10
15	8	PE Solprene PE- (33% core layer)	5 mils (127 $\mu$ m)	01 100 300	15
	9	PE Kraton 2109 PE- (33% core layer)	5 mils (127 $\mu$ m)	500 0 100	
	20	PE EVA Kraton 2109 (33% core layer)	5 mils (127 $\mu$ m)	300 500 0 100	
25	10	PE EVA Kraton 2109 (33% core layer)	5 mils (127 $\mu$ m)	300 500 0 100	20
	11	Plexar 3 PEBAK 2533 Plexar 3 (90% core layer)	4 mils (102 $\mu$ m)	500 0 100 300	
	30	Plexar 3 PEBAK 3533 Plexar 3 (35% core layer)	6.9 mils (175 $\mu$ m)	500 0 100 300 500	

35 PE - Chemplex 3404-D obtained from Chemplex Corp.; Solprene - solprene 418 obtained from Phillips Chemical

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PE - Chemplex Plexar copolymer.

PE - Chemplex 3404-D; EVA - Chemplex 3312

Plexar 3 is trade name of Chemplex Corp.

TABLE I (Continued)

	Sample No.	% Permanent Deformation	% Heat Shrinkage	Hysteresis Ratio (HR)	
5	8	...	0.6	3.6	5
		10.2	6.3	3.4	
		90.9	25.1	3.1	
10		74.2	20.0	1.7	10
	9	...	1.6	3.9	
		11.2	7.6	3.9	
		111.4	25.1	3.4	
		103.7	17.8	2.1	
15	10	...	0.6	3.1	15
		5.5	6.7	2.8	
		58.7	34.7	2.1	
		71.9	29.9	2.0	
20	11	...	0.8	1.75	20
		4.8	3.5	1.74	
		115.2	43.7	1.53	
		277.0	60.4	1.61	
	12	...	0.8	3.81	
25		12.1	8.2	3.36	25
		177.2	43.1	3.63	
		376.0	51.3	4.00	

TABLE II (Continued)

	Sample No.	Film (Outer layer core /layer outer layer)	Extruded Film Thickness	% Stretch	
30	13	EVA PEBAX 2533	3.6 mils	0	30
35		EVA: (74% core layer)	(91 $\mu$ m)	100 300	35
40	14	Plexar 3 PEBAX 3533 Plexar 3 (67% core layer)	4.9 mils (124 $\mu$ m)	500 0 100 300	40
45	15	Plexar 3 PEBAX 4033 Plexar 3 (66% core layer)	3.4 mils (86 $\mu$ m)	500 0 100 300 500	45

\*EVA = Chomplex 4634

TABLE II (Continued)

5	Sample No.	% Permanent Deformation	% Heat Shrinkage	Hysteresis Ratio (HR)	5
	13	...	0.6	2.04	
		4.8	3.6	2.05	
10		129.1	46.5	2.35	
		289.0	61.4	2.18	10
	14	...	2.6	2.18	
		7.5	5.9	2.07	
		160.9	44.7	2.17	
15	15	309.0	56.1	2.30	
		...	0.4	3.19	15
		14.3	5.6	3.11	
		181.8	34.9	3.81	
		349.0	42.9	4.19	

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*Example III*

Example II was repeated with the exceptions that Plexar 102 (commercially available from the Chemplex Corp.) and Surlyn-1702 (commercially obtained from DuPont) were utilized as outer layers in 10% 20% 10% relative volume compositions (i.e. outer layer core layer outer layer) with a core layer of PEBAK 25 2533 and 3533. Testing for percent heat shrinkage and hysteresis ratio were conducted as in Example I and the results thereof are tabulated in Table III below.

TABLE III

30	Sample No.	Film (Outer layer core layer outer layer)	Extruded Film Thickness	% Stretch	30
35	16	Plexar 102 Pebax-2533 Plexar 102* (10 80 10)	3 mils (76 $\mu$ m)	100 200 300 400	35
40	17	Surlyn 1702 Pebax-3533 Surlyn 1702** (10 80 10)	3 mils (76 $\mu$ m)	500 100 200 300 400	40
45	18	Plexar 102 Pebax-3533 Plexar 102 (10 80 10)	3 mils (76 $\mu$ m)	500 100 200 300 400	45
50	19	Plexar 102 Pebax-3533 Plexar 102 (10 80 10)	2 mils (51 $\mu$ m)	500 100 200 300 400 500	50

\* Plexar 102 is an ionomer resin commercially available from Chemplex Corp.

\*\* Surlyn 1702 is an ionomer resin commercially available from duPont de Nemours Co.

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TABLE III (Continued)

Sample No.	% Permanent Deformation	% Heat Shrinkage	Hysteresis Ratio (HR)	
5				5
16	7	5	2.20	
	60	28	2.32	
10	142	36	1.93	
	225	43	2.09	10
	277	51	1.71	
17	5	6	2.43	
	37	22	2.06	
15	102	43	2.26	
	179	52	2.25	15
	265	62	2.15	
18	6	4	1.73	
	42	19	1.80	
20	120	34	1.68	
	208	47	1.76	20
	269	52	1.56	
19	7	5	2.30	
	53	23	1.91	
	104	33	2.04	
25	224	39	1.66	
	266	51	1.90	25

From the above examples, it is readily apparent that both the single layer and coextruded PEBAX films exhibit satisfactory results in percent heat shrinkability (e.g. between about 30-70%) when stretched to 30 elongation values of between about 200% to about 500% so that, when applied to the waistbands of disposable diapers, for example, adequate shirring is achieved. For most of the tested films, the percent heat shrinkability decreased as the percent film stretch increased from 300% to 500%, while in direct contrast, the films of this invention increased in percent heat shrinkage as the film stretch increased from 300% to 500% (e.g. compare sample Nos. 4-5 to 1-2; 8-10 to 11-19). Sample Nos. 3 and 6, although increasing somewhat in percent heat shrinkability did not exhibit the requisite heat shrinkability useful for elastically shirred articles. Thus, the films of the present invention now make it economically feasible to produce disposable diapers having elastic waistbands which exhibit the necessary amount of heat shrinkability to achieve sufficient shirring. Moreover, the films of the present invention overcome many of the commercial and production disadvantages of conventional heat-shrinkable elastomers since no heat setting is required in order to achieve the above-described advantages.

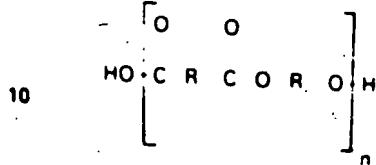
## CLAIMS

1. A method of producing a heat-shrinkable elastomer comprising the steps of:
  - (a) without the application of external heat, extending an elastomer comprising a copolymer of alternating polyamide and polyether repeat block polymer segments to an extension beyond that at which permanent deformation occurs thereby to orient said elastomer uniaxially, and
    - (b) subsequently releasing the tension on said elastomer to allow natural relaxation thereof to a linear density substantially above the minimum linear density achieved in the extension of step (a) and substantially below that of said elastomer before the extension of step (a).
2. A method as claimed in claim 1 comprising the steps of:
  - (a) uniaxially orienting an elastomer of a first length consisting essentially of a copolymer of alternating polyamide and polyether repeat block polymer segments, said orienting being conducted without the application of external heat to uniaxially orient said elastomer to a second length substantially greater than a third length at which permanent deformation of said elastomer occurs; and
    - (b) releasing the uniaxial tensioning applied according to step (a) to allow said elastomer to naturally relax to said third length which is substantially greater than said first length.
3. A method as claimed in either of claims 1 and 2 wherein said elastomer is extruded to at least about 200% elongation to achieve uniaxial orientation thereof.
4. A method as claimed in claim 3 wherein said elastomer is extended to from about 200% to about 700% elongation to achieve uniaxial orientation thereof.
5. A method as claimed in any one of claims 1 to 4 wherein prior to step (a) a core of said elastomer is provided with an outer layer of an extendable nonelastomer.
6. A method as claimed in claim 5 wherein said core is in layer form disposed between outer layers of said non-elastomer.

7. A method as claimed in claim 6 wherein prior to step (a) said outer layers and said core are formed by melt lamination.

8. A method as claimed in any one of claims 5 to 7 wherein said core forms from about 70% to about 90% of the total by weight of said core and said outer layers.

5 9. A method as claimed in any one of the preceding claims wherein said copolymer has the formula



wherein R<sub>1</sub> is a polyamide residue selected from nylon 6, nylon 10, nylon 11, nylon 12 and nylon 6, 6 15 residues; R<sub>2</sub> is a polyether residue selected from polyethylene glycol, polypropylene glycol and polytetra- 15 methylene glycol residues; and n is an integer.

10. A heat-shrinkable elastomer whenever produced by a method as claimed in any one of claims 1 to 9.

11. A heat-shrinkable elastomer as claimed in claim 10 wherefor the minimum linear density achieved 20 in the uniaxial deformation of step (a) is from about 40 to about 60% of the linear density achieved on the subsequent relaxation.

12. A heat-shrinkable elastomer as claimed in claim 10 comprising an elastomeric core layer disposed 25 between non-elastomeric outer layers and wherefor the minimum linear density achieved in the uniaxial deformation of step (a) is from about 20 to about 60% of the linear density achieved on the subsequent relaxation.

13. A process for producing an elastomer which comprises the step of:  
(c) heat-shrinking a heat shrinkable elastomer as claimed in any one of claims 10 to 12.

14. A process as claimed in claim 13 which comprises exposing said heat-shrinkable elastomer to mi- 30 crowave energy.

30 15. An article having a portion thereof elastically shirred by the attachment thereto of a heat shrunk elastomer produced according to a process as claimed in either of claims 13 and 14.

16. A process of elasticating an article comprising affixing to said article a heat-shrinkable elastomer as claimed in claim 10.

17. A process as claimed in claim 16 further comprising the step of heat shrinking the affixed elastomer to cause shirring of said article.

35 18. A process as claimed in claim 17 wherein said heat shrinking is conducted by means of micro- wave energy.